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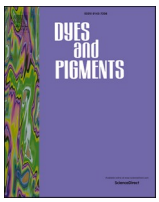

Synthesis and characterization of a unique fused spiro-dihydropyran based chemodosimeter for selective visual and fluorescent detection of Cu^{2+} ion in aqueous medium by "turn-on" mode

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ABSTRACT

A realistically newly designed Cu^{2+} ion specific fluorescent chemodosimeter has been synthesized from α,α'-(*E*, *E*)-bis(benzylidene)cyclohexanone having a fused spiro-dihydropyran moiety characterized by 2D NMR and X-Ray Crystallographic study. It also demonstrates an irreversible, instant direct visualisation by unaided eye chemosensing property in aqueous buffer (pH 7.4) with a colour change from yellow to orange upto 0.3×10^{-6} M.

1. Introduction

In the last few years the construction and development of highly selective and sensitive fluorescent sensors and chemodosimeters which are mostly multifunctional organic compounds for copper-ions have gained substantialinterest [1]. Focus on the design and synthesis of such multifunctional organic compounds as new fluorescent probes for different metals with controllable molecular characteristics is the essential goal of chemistry [2]. Sensing materials depend on several photophysical phenomena such as photo-induced electron transfer and intramolecular charge transfer among others [3]. In the new era, chromogenic sensing units have received a lot of interest when comparing to fluorescence sensors because they are able to detections with just by the human eye and no additional expensive instruments were required. Designing new varieties of host molecules with the ability to sense cations and anions by the unaided eye is a substantial area of interest. Among the essential metals in humans; copper, a trace element, which acts a very important role in various biological and environmental processes [4]. At the same time augmented and deficiency level of copper ion causes severe diseases like Parkinson's, Menke's, Wilson's Alzheimer's diseases and idiopathic copper toxicosis syndrome caused by accumulation of Cu^{2+} in the liver [5]. Beside this, Cu^{2+} ion can also cause gastrointestinal disorder, cardiovascular disease and diabetes [6]. As said by the U.S. Environmental Protection Agency (EPA), less than 1.3 ppm concentration of Cu^{2+} ion are acceptable in drinking water. Therefore, the design of various methods to track the concentration of Cu^{2+} in various samples and visualize its cellular distribution in physiological processes is extremely important for the preservation of the environment and for maintaining human health.

Moreover, copper is paramagnetic and resulted in quenching of luminescence of the investigating fluorescence probe [7]. But these types of "turn-off" probes reported in the literature suffer from limitations, for example low sensitivity and the change in the fluorescence intensity with varying environment (temperature, polarity, pH) [8]. On the other hand, reaction based fluorescent sensors with "turn-on" signals usually have higher sensitivity and better selectivity owing to obvious structural changes caused by specific chemical reactions [1e]. So far most of the chemodosimeters found in literature are generally converting non-emissive to emissive probes by means of irreversible pathways involving hydrolysis of esters and amides, oxidations, oxidative cyclization, dethioacetalizations promoted by copper ions [9]. Chemodosimeters reported earlier with core moieties based on benzimidazoles 10a,b, dihydropyrazine [10c], naphthalimide [10d], rhodamine 10e,f, dicyanoisophorone [10g], phenothiazine [10h], fluorescein [9c] andthiazoloquino-xaline [9b] for detection of copper ions.We would like to introduce a highly selective, sensitive spiropyran based chemodosimeter for copper ion detection via irreversible "turn-on" fluorescent mode with instant visual color change in aqueous medium.

Single Electron Transfer (SET) reactions dominate many interesting research fields like Supramolecular chemistry, organometallics,

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